

121325-1

## IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

APPLICANT:	Kevin G. Harding	)
		) Group Art Unit: 2656
SERIAL NO.:	10/065,882	)
		)
FILED:	11/27/2002	) Before the Examiner:
		) Christopher Ray Lamb
FOR:	MULTI-LAYER HOLOGRAPHIC	)
	DATA RECORDING METHOD	)

Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

**DECLARATION UNDER 37 CFR 1.132**

I, Mr. Kevin G. Harding, declare that:

1. I have read and fully understand the above-referenced U.S. patent application, herein referred to as "the application."
2. I graduated from University of Rochester with a Masters Degree in Optical Engineering in 1978. From 1978 to present, I have been an Optical Research Engineer, working extensively in the fields of interferometry, optical metrology, holography and optical instrumentation. I have greater than 27 years of experience as an Optical Research Engineer.
3. I have reviewed the Office Action mailed 03/20/2006, wherein the Examiner has rejected all pending claims. In the Office Action, the Examiner has asserted that "memory access media" "are not sufficiently described in the specification to enable one skilled in the art to which it pertains to make and/or use the invention without undue experimentation."

121325-1

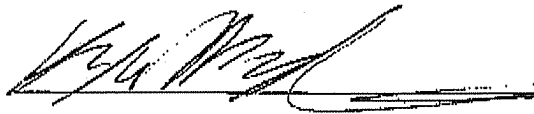
As one skilled in the art, I declare that:

4. The claims of the pending application relate to holographic data recording media in multiple layer arrangements.
5. At the time of the filing of the application, holographic data recording media were known to those skilled in the art. Exemplary disclosures describing holographic data recording media include:
  - A. "Holographic storage in conjugated-polymer composites" Ofer Levi, Galina Perepelitsa, and Dan Davidov Racah, Aharon J. Agranat, Iris Benjamin, Shoshy Shalom, and Ronny Neumann, Yair Avny, The Hebrew University of Jerusalem, Givat Ram, Jerusalem 91904, Israel Phys. Rev. B 57, R12647-R12650 (1998);
  - B. "Organic storage media for holographic optical memory: state-of-the-art and future" Valery A. Barachevsky; Proc. SPIE Vol. 4149, p. 205-212, Holography 2000; Tung H. Jeong, Werner K. Sobotka; Eds.; and
  - C. "Digital Holographic Data Storage in a High-Performance Photorefractive Polymer Composite," M.D. Rahn, D.P. West, K. Khand, J.D. Shakos, R.M. Shelby. Applied Optics, Vol. 40, No. 20, (10 July 2001).
6. The materials disclosed in the foregoing exemplary publications are suited to practice of the invention disclosed in the application, without undue experimentation by one skilled in the art.

121325-1

7. I declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the patent.

Date: 5/16/2006



Mr. Kevin G. Harding

**Acknowledgement Receipt**

The USPTO has received your submission at **15:01:31** Eastern Time on **17-MAY-2006**.

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**eFiled Application Information**

EFS ID	1049926
Application Number	10065882
Confirmation Number	5283
Title	MULTI-LAYER HOLOGRAPHIC DATA READING
First Named Inventor	Kevin George Harding
Customer Number or Correspondence Address	23413
Filed By	Ira M. Turner/Tracy Axiak
Attorney Docket Number	121325-1
Filing Date	27-NOV-2002
Receipt Date	17-MAY-2006
Application Type	Utility

**Application Details**

Submitted Files	Page Count	Document Description	File Size	Warnings
US_IDS_Form__SB_08a.pdf	4	Information Disclosure Statement (IDS) Filed	723173 bytes	⚠ WARNINGS

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**INFORMATION DISCLOSURE  
STATEMENT BY APPLICANT**  
( Not for submission under 37 CFR 1.99)

Application Number	10065882
Filing Date	2002-11-27
First Named Inventor	Kevin George Harding
Art Unit	2652
Examiner Name	Christopher Ray Lamb
Attorney Docket Number	121325-1

**U.S.PATENTS**

Examiner Initial*	Cite No	Patent Number	Kind Code <sup>1</sup>	Issue Date	Name of Patentee or Applicant of cited Document	Pages, Columns, Lines where Relevant Passages or Relevant Figures Appear
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**U.S.PATENT APPLICATION PUBLICATIONS**

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**FOREIGN PATENT DOCUMENTS**

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**NON-PATENT LITERATURE DOCUMENTS**

Examiner Initials*	Cite No	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc), date, pages(s), volume-issue number(s), publisher, city and/or country where published.	T <sup>5</sup>

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Application Number	10065882
Filing Date	2002-11-27
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Attorney Docket Number	121325-1

1	Rahn, et al. "Digital holographic data storage in a high-performance photorefractive polymer composite". 10 July 2001/ Vol. 40, No. 20/ APPLIED OPTICS pp. 3395-3401	<input type="checkbox"/>
2	Barachevsky, V.A. "Organic Storage Media for Holographic Optical Memory: State-of-the-art and Future". SPIE Vol. 4149 (2000) pp. 205-212	<input type="checkbox"/>
3	Levi, et al. "Holographic Storage in conjugated-polymer composites" Physical Review B, Condensed Matter and Materials Physics" Third Series, Vol. 57, No. 20. 15 May 1998-II. 4 pages	<input type="checkbox"/>

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STATEMENT BY APPLICANT**  
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Application Number	10065882
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Art Unit	2652
Examiner Name	Christopher Ray Lamb
Attorney Docket Number	121325-1

**CERTIFICATION STATEMENT**

Please see 37 CFR 1.97 and 1.98 to make the appropriate selection(s):

- ☐ That each item of information contained in the information disclosure statement was first cited in any communication from a foreign patent office in a counterpart foreign application not more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(1).

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- ☐ See attached certification statement.
- ☐ Fee set forth in 37 CFR 1.17 (p) has been submitted herewith.
- ☐ None

**SIGNATURE**

A signature of the applicant or representative is required in accordance with CFR 1.33, 10.18. Please see CFR 1.4(d) for the form of the signature.

Signature	/Ira M. Turner/	Date (YYYY-MM-DD)	2006-05-17
Name/Print	Ira M. Turner	Registration Number	53887

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# Digital holographic data storage in a high-performance photorefractive polymer composite

Mark D. Rahn, David P. West, Kaleemullah Khand, John D. Shakos, and Robert M. Shelby

Binary information in the form of a  $256 \times 256$  pixel array has been stored holographically within a polymeric photorefractive composite of 130- $\mu\text{m}$  thickness. Devices used consisted of 55-wt. % organic chromophore 1-(2'-ethylhexyloxy)-2,5-dimethyl-4-(4"-nitrophenylazo) benzene and up to 11.2-wt. % 2,4,7-trinitro-9-fluorenone (TNF) dispersed within a poly(*N*-vinyl carbazole) matrix. In a degenerate four-wave mixing arrangement, the refractive-index modulation and speed were  $10^{-3}$  and 200 ms, respectively. The high TNF concentration leads to short digital hologram recording times of 2 s without detriment in optical quality. Although not yet optimized, a figure of merit, *M*#, for holographic storage in this composite has been measured to be 0.017, and this is estimated to reach 0.18 in a revised experimental geometry. © 2001 Optical Society of America

OCIS codes: 210.2860, 190.5330, 160.4330, 160.4890, 160.5470.

## 1. Introduction

Digital holographic data storage is an active field of research because of the potential advantages of a holographic storage system,<sup>1</sup> including high storage density and extremely fast data retrieval rates through parallel readout of an entire data page.<sup>2-4</sup> Furthermore, optical computing technologies, which are the subject of much research, will require some form of optical data storage. Another advantage of holographic data storage is that it is content rather than address searchable, making it more useful for archive or optical correlation applications.<sup>5</sup>

In laboratory demonstrations, contemporary erasable magnetic disk technology has achieved an areal density of approximately 8 Gbits/cm<sup>2</sup>. Achievable areal density of information on magnetic disks has historically increased exponentially<sup>6</sup> over time with

many difficult engineering obstacles defeated on the way. Several technical problems now threaten to limit this growth rate at some time in the next few years.<sup>6</sup> Laboratory demonstrations of optical holographic data-storage systems have already shown a similarly large storage density,<sup>7</sup> whereas projections of storage density in future holographic storage systems exceed 20 Gbits/cm<sup>2</sup>. Holographic data retrieval rates between 1 and 8 Gbits/s have been demonstrated.<sup>3,4</sup>

The attractiveness of photorefractive materials for holographic data storage lies in their read-write capability.<sup>8</sup> In photorefractive storage media an optical pattern inside the material, created by interference between a reference and a data-containing object beam, results in a patterned generation of mobile charges and corresponding charge generation sensitizer ions. Drift of mobile charges under an external poling field (or diffusion) and subsequent recombination with sensitizer ions results in charge separation and a space-charge field. A refractive-index hologram is thus formed by the electro-optic effect.<sup>9</sup> The spatial distribution of charge can be equilibrated by uniform illumination by the reference beam only or with an incoherent white-light source, thereby erasing the hologram ready for subsequent hologram recording. Although the details of the charge generation,<sup>10</sup> drift,<sup>11</sup> trapping,<sup>12-14</sup> and nonlinear<sup>15</sup> processes all differ in polymeric photorefractive materials compared with inorganic photorefractive crystals, many aspects of

When this research was performed, M. D. Rahn, D. P. West, K. Khand, and J. D. Shakos were with the Laser Photonics Research Group, Department of Physics and Astronomy, Manchester University, Manchester M13 9PL, United Kingdom. M. D. Rahn (m.rahn@sheffield.ac.uk) is now with the Department of Physics and Astronomy, University of Sheffield, Sheffield S3 7RH, United Kingdom. R. M. Shelby is with the IBM Research Division, IBM Almaden Research Center, 650 Harry Road, San Jose, California 95120-6099.

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the standard model of photorefractivity are applicable,<sup>16</sup> and inexpensive polymeric devices can be prepared with basic procedures.

To date, no material is known with all the required properties for a rewritable photorefractive holographic storage system with competitive performance. Almost all the available photorefractive materials do not have a sufficient dynamic range. Crystals do not necessarily require a high external poling field, so a thick crystal can be used to store many holograms, but the refractive-index modulation is smaller than that achievable with photorefractive polymers. Polymeric materials have a high refractive-index modulation, but the requirement of an external poling field precludes use of simple devices much thicker than 200  $\mu\text{m}$ , meaning that the storage density achievable in crystals is currently higher in thick crystals despite a lower refractive-index modulation. The essential requirement of high optical quality has resulted in practical demonstrations of digital holographic storage in photorefractive polymers being limited to glassy materials with a very long hologram growth time, greater than 20 s, under typical conditions used for digital holographic storage.<sup>17-19</sup>

Many organic photorefractive materials have shown excellent holographic performance in an optimized degenerate four-wave mixing (DFWM) arrangement. Notable achievements are a refractive-index modulation in the range of  $2\text{--}5 \times 10^{-3}$  (Ref. 20) and some very fast response times with the fastest response speed now under 1 ms.<sup>21</sup> The response speed of a photorefractive polymer is limited ultimately by the requirement for charge photogeneration. In some photorefractive polymers this limit is not reached because some other processes contributing to grating formation are slower. Both the charge generation rate and the refractive-index modulation obtained with any specific material are strongly dependent on the experimental parameters of the applied electric field and the intensity contrast of the interference pattern formed by the holographic writing beams. The speed and refractive-index modulation of a material observed in DFWM or two-beam coupling arrangements therefore cannot be compared with those observed in a digital holographic storage arrangement. This is due to additional constraints on the experimental arrangement in the digital case that are detailed in this paper.

We report here on digital holographic storage using a previously reported photorefractive polymer.<sup>22</sup> In an optimized (DFWM) arrangement, this polymer shows a refractive-index modulation of  $1 \times 10^{-3}$  and a response speed of 200 ms when we use an applied field of  $50 \text{ V } \mu\text{m}^{-1}$  and an average intensity of  $400 \text{ mW cm}^{-2}$ . This yields the figure of merit  $p = \Delta n / E^2$ , the refractive-index modulation divided by the applied field squared, of  $4 \times 10^{-7} \mu\text{m}^2 \text{ V}^{-2}$ .<sup>23</sup> The experimental conditions that we used were rather modest in comparison with those that were used in the literature to collect the best dynamic performance data for photorefractive polymers, wherein higher

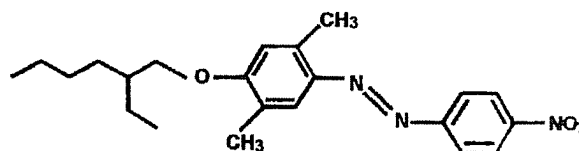


Fig. 1. EHDNPB electro-optic chromophore.

fields and larger intensity contrasts of, for example,  $76.5 \text{ V } \mu\text{m}^{-1}$  and  $1.44 \text{ W cm}^{-2}$ , respectively, were used.<sup>21</sup> An image of a 64-kbit digital array is transmitted without error, which is an indication of good optical quality. Such optical quality is maintained in a device for over two years. These properties are all combined within a single material, so the overall performance of this material in digital data storage represents a good benchmark for the current status of photorefractive polymers.

We achieved high optical quality by using the crystallization-resistant chromophore 1-(2'-ethylhexyloxy)-2,5-dimethyl-4-(4'-nitrophenylazo) benzene (EHDNPB)<sup>18</sup> (Fig. 1). The ethylhexyl aliphatic end group imparts crystallization resistance and permits high optical quality composites to contain up to 55-wt. % chromophore. The high chromophore concentration results in a high refractive-index modulation that is approximately  $10^{-3}$  in a typical DFWM geometry.<sup>22</sup> Fast recording speeds were achieved by use of relatively high concentrations (11 wt. %) of the charge-generating species 2,4,7-trinitro-9-fluorenone (TNF) without detriment in optical quality.

## 2. Holographic Storage Device Construction

We prepared high optical quality devices by mixing the solid constituents of the composite in dichloromethane and casting the mixture onto glass sheets containing indium tin oxide electrodes. After allowing ample time for evaporation of the dichloromethane by holding the plates at  $135^\circ\text{C}$ , we pushed the two plates together, squeezing the molten plastic mixture in between. Plastic spacers are placed between the plates to ensure uniform thickness. After assembling, we heated the device again to  $135^\circ\text{C}$  for 2 h to homogenize the material before allowing it to cool slowly. The area of electrode overlap forming the useful aperture for the object and reference beams was roughly circular with a 4-mm diameter. The useful aperture could not be increased without a reduction in optical quality because of homogenization difficulties. Holographic storage is reported for a device with 54.3-wt. % EHDNPB, 11.2-wt. % TNF, and 34.5-wt. % poly(*N*-vinyl carbazole) (PVK). The thickness of the polymer layer was  $d = 130 \mu\text{m}$ , so an applied voltage of 6.5 kV provided an external poling field of  $50 \text{ V } \mu\text{m}^{-1}$ .

## 3. Digital Holographic Storage Tests

Digital holographic storage tests were conducted essentially as described previously<sup>17,24</sup> with a  $\text{Kr}^+$  laser ( $\lambda = 676 \text{ nm}$ ) for hologram recording and retrieval. Digital holograms were formed by an interference

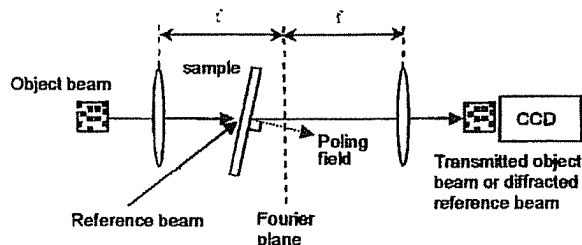


Fig. 2. Schematic of the holographic storage optical arrangement showing the incoming object and reference beams and the corresponding transmitted and diffracted beams. During the recording process, an object beam is combined with a reference beam in the sample. During readout of the hologram, an object beam is not used, and the reference beam is diffracted into the detector.

between a *p*-polarized object and reference beams (Fig. 2). The object beam was passed through a random 64-kbit data mask consisting of a  $256 \times 256$  array of  $18\text{-}\mu\text{m}$ -square pixels on  $36\text{-}\mu\text{m}$  spacing, with half of the pixels transmissive to encode binary 1 and half opaque to encode 0. The data-encoded masked beam was then focused by an  $f = 8.5\text{-cm}$  focal-length lens. At a distance of  $8.5\text{ cm}$  behind the Fourier plane, another  $8.5\text{-cm}$  focal-length lens recollimated the object beam so that the transmitted image could be collected by a CCD array with a  $9\text{ }\mu\text{m} \times 9\text{ }\mu\text{m}$  pixel size. In this arrangement each reconstructed image pixel covered four pixels on the CCD array. The sample was placed approximately  $20\text{ mm}$  in front of the Fourier plane to avoid saturation by the bright spots in the Fourier transform of the mask pattern corresponding to light from many pixels adding constructively in space. Prior to hologram recording, the image quality of the data mask was obtained first in transmission. Taking this image allowed us to check on the optical quality of the device.

The collimated reference beam was incident on the same area of the sample, and its angle of incidence was varied to allow multiplexing of more than one hologram into the device. Table 1 summarizes the

details of the experimental arrangement used for hologram recording and data retrieval and the results obtained. We achieved data retrieval using a reference beam controlled by a shutter to limit the exposure time, thus avoiding unnecessary hologram erasure and CCD saturation. The diffracted reference beam is colinear with the transmitted object beam, and we can image it onto the CCD array in the same way as the transmitted data image without readjusting the optical system.

Either the reference beam diffracted by the hologram or the transmitted image of the masked object beam could be imaged onto the CCD array. We analyzed the quality of the reconstructed image of the data mask, either in transmission or by diffraction off the hologram, by measuring the signal given by each pixel group. Comparison of the image with the original data mask allowed the presence of false ones and zeros to be interpreted as errors. The quality of the transmitted image obtained is shown in Fig. 3. To interpret the histograms, the reader is referred to the legend in Fig. 3. Apart from two persistent errors that may have resulted from dust on the data mask, an error-free image was received in transmission through the device. Figure 4 represents the image quality of the reference beam diffracted off a hologram recorded in the device. Although the transmitted image was virtually without error, 21 errors were encountered when we analyzed the diffracted reference beam. This corresponds to a raw bit error rate of  $3.2 \times 10^{-4}$ . When modulation and error-correction coding techniques are utilized,<sup>5</sup> this raw bit error rate is small enough for information storage and retrieval at error rates of  $10^{-12}$  or better with some loss ( $\sim 30\text{--}40\%$ ) of storage density.

The data input rate in a holographic storage device for a given set of experimental parameters is limited by the sensitivity of the material, which is a material property proportional to the refractive-index modulation per unit exposure. It is most easily determined in a simpler plane-wave diffraction

Table 1. Experimental Parameters and a Summary of the Measured Hologram and Reconstructed Image Data

Parameter	54.3% EHDNPB, 11.2% TNF, and 34.5% PVK
Object beam intensity on device ( $\text{mW cm}^{-2}$ )	1.12
Reference beam intensity on device ( $\text{mW cm}^{-2}$ )	85.7
Intensity contrast of the interference pattern, $m$	0.214
Object beam external angle with respect to device normal	$20^\circ$
Reference beam external angle with respect to device normal	$60^\circ$
Reference beam intensity for data retrieval and erasure ( $\text{mW cm}^{-2}$ )	85.7
Hologram recording time (s)	2
Hologram readout time (s)	0.005 <sup>a</sup>
Sensitivity ( $\text{cm/J}$ )	50
Image contrast	10.14 <sup>b</sup>
Diffraction efficiency, $\eta$	$1.89 \times 10^{-4}$
Holographic refractive-index modulation, $\Delta n$	$2.4 \times 10^{-5}$
Errors	21
Raw bit error rate	$3.2 \times 10^{-4}$

<sup>a</sup>See Fig. 5.

<sup>b</sup>Defined as the mean of 1 pixel divided by the mean of 0 (see Figs. 3 and 4).

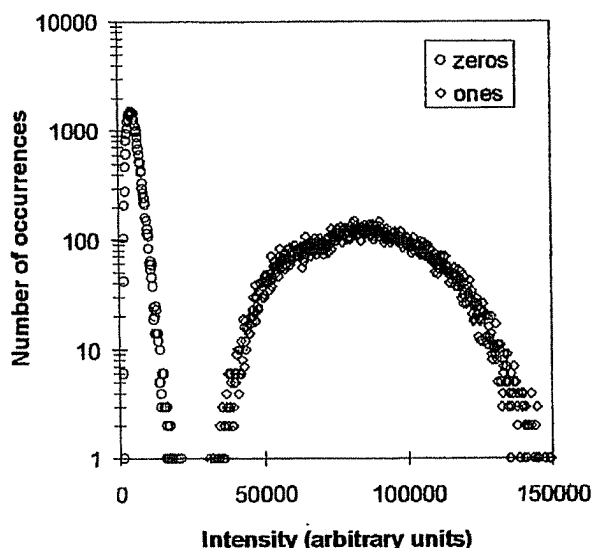


Fig. 3. Histogram representing the quality of the image of the transmitted object beam through the sample containing 11.2% TNF. The horizontal axis depicts values of the CCD pixel signal, and the vertical axis depicts the number of pixels having that signal level. Circles represent those pixels that were expected to be zeros, and diamonds represent the pixels that were expected to be ones. The threshold between interpretation as a zero and a one lies at the center of the overlap between the two peaks on the histogram. Zeros occurring with a higher signal than the threshold value, or ones occurring with a lower signal, give an error. The image histogram has no overlap and therefore no errors.

experiment, in which two collimated beams write and read a grating in the material. However, we can estimate the observed sensitivity by taking into account the more complex structure of a data-bearing object beam in a simple approximate way by introducing the fringe visibility of the interference pattern

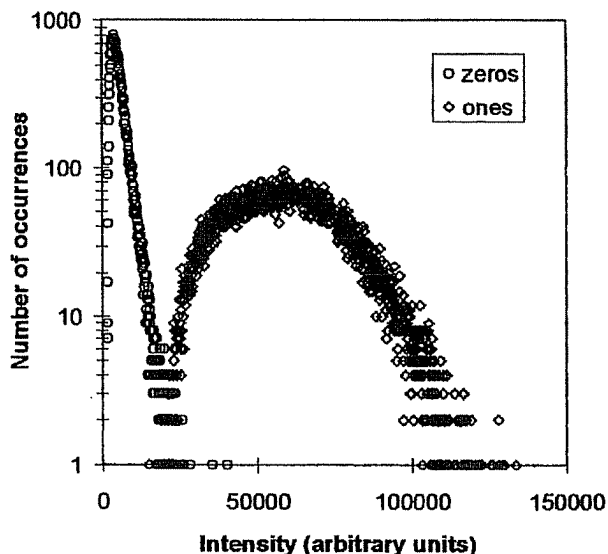


Fig. 4. As in Fig. 3 but for the image of the diffracted reference beam off a hologram stored in a device containing 11.2% TNF.

formed in the material by the reference and object beams. This is defined as

$$m = \frac{2 \cos 2\phi \sqrt{I_R I_O}}{(I_R + I_O)}, \quad (1)$$

where  $I_O$  and  $I_R$  are the average object and reference intensities, and the internal angle between the object and the reference beams is  $2\phi$ . It is also convenient to use the square root of diffraction efficiency divided by the interaction length as a measure of the index modulation. This results in a sensitivity definition of

$$S = \frac{\sqrt{\eta}}{(mItl)}, \quad (2)$$

where  $\eta$  is the diffraction efficiency defined as the ratio of the total diffracted power to the total incident reference beam power,  $I$  is the total intensity during writing,  $t$  is the writing time, and  $l$  is the interaction length in the material. With these definitions, we find 50 cm/J for the sensitivity of the material.

#### 4. Multiple Hologram Storage

The number of holograms  $M$  that can be multiplexed within a holographic storage medium is given by

$$M = \frac{M\#}{\sqrt{\eta_m}}, \quad (3)$$

where  $M\#$  is a parameter dependent on the material properties, the thickness of the device, the fringe visibility, the intensity of writing beams, the applied electric field, and the geometry used for hologram storage.<sup>25</sup>  $\eta_m$  is the minimum diffraction efficiency required to read out each hologram with a sufficiently low bit error rate. The parameter  $M\#$  is given by<sup>25</sup>

$$M\# = W\tau_d. \quad (4)$$

Here  $W$  is the linear growth rate in the small exposure limit  $d/dt(\sqrt{\eta})$  and  $\tau_d$  is the exposure time required to reduce  $\sqrt{\eta}$  by  $1/e$ . The optical intensities used for digital hologram recording and erasure must be used for this measurement.

A hologram with a diffraction efficiency of  $2.26 \times 10^{-4}$  was recorded in 5 s, which yields  $W = 0.003$ . Figure 5 shows the decay of a hologram in this device and gives  $\tau_d = 5.7$  s. Equation (2) therefore yields  $M\# \sim 0.017$ . One recorded hologram with a fairly low diffraction efficiency of  $8.3 \times 10^{-5}$  had a reasonable raw bit error rate of  $9.2 \times 10^{-4}$  and provides us with  $\eta_m$ . The number of holograms that can be multiplexed in this sample by use of the experimental geometry described in Table 1 is therefore  $M \sim 2$ . Indeed, two holograms were stored successfully in this device, but storage of a third erased the first to below the contrast required for low error rate retrieval. This level of performance is not sufficient to be of use in commercial applications in which the goal is to find a holographic storage device with  $M\# = 1$  or

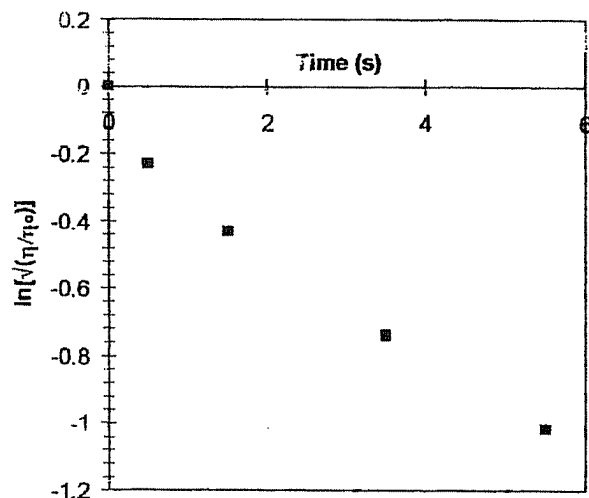


Fig. 5. Graph showing the erasure of a hologram when exposed to the 85.7-mW reference beam. The natural log of the square root of the diffraction efficiency normalized by its initial value ( $\ln \sqrt{\eta/\eta_0}$ ) is plotted against the time exposed to the reference beam. The characteristic erasure time  $\tau_d$  is given when  $\ln \sqrt{\eta/\eta_0} = -1$ .

greater, a factor of approximately 50 higher than that achieved here.

### 5. Comparison of Degenerate Four-Wave Mixing and Digital Data Storage

The holographic storage performance described can be improved when the experimental parameters are changed: Optimized storage geometry was not possible in this study because of the small effective aperture for the object beam. This limited the maximum angle the object beam could subtend with the device normal. Devices constructed with a larger area were found to have reduced optical quality.

Holograms formed in a DFWM arrangement, however, can be written in the material with almost any geometry. The refractive-index modulation that we achieved using a plane-wave object beam in an optimized geometry therefore can be related to that achieved in a real storage system with a masked object beam.

A calculation of the amplitude of the refractive-index modulation ( $\Delta n$ ), achieved for digital data storage according to Table 1, yields  $\Delta n = 2.4 \times 10^{-5}$  from a measured diffraction efficiency of  $\eta = 1.89 \times 10^{-4}$ . This calculation uses the relation

$$\Delta n = \frac{\lambda_v (\cos \theta_1 \cos \theta_2)^{1/2}}{\pi d \cos(\theta_2 - \theta_1)} \sin^{-1}[\eta/\exp(-\alpha l)]^{1/2}, \quad (5)$$

where  $\theta_1$  and  $\theta_2$  are the internal angles from normal incidence of the reference and object beams, respectively;  $\alpha = 3.5 \text{ cm}^{-1}$  is the attenuation coefficient of the polymer at 676 nm; and  $\lambda_v$  is the wavelength of the beams in free space.<sup>26</sup>

In a separate DFWM arrangement, a hologram was recorded and the refractive-index modulation  $\Delta n$

was measured with the same geometry, field intensity, and fringe visibility as was used for digital data storage. This was therefore a nonoptimized DFWM arrangement. A wavelength  $\lambda_v = 680 \text{ nm}$  was used, and the object beam was a plane wave, i.e., not passed through a data mask. A diffraction efficiency of  $\eta = 1.8 \times 10^{-3}$  was observed, which indicates [by use of Eq. (5)] that a refractive-index modulation  $\Delta n = 6.1 \times 10^{-5}$  was obtained. This modulation is a factor 2.5 higher than the modulation obtained with a masked object beam under the same conditions.

This discrepancy probably arises because the fringe visibility of the interference pattern  $m$  may be lower in the case of a masked, spatially patterned object beam than the value of 0.214 calculated for a plane-wave object beam by use of Eq. (1). Also, when a masked object beam is used, larger intensity gradients can be formed at points within the polymer. The space-charge field is a function of the intensity gradient and is limited by the density of charge trapping sites within the photorefractive polymer. Such a reduction, however, has not been observed when tested with variable angle DFWM measurements up to an external angular separation of  $40^\circ$  between the object and the reference beams.

It is useful to estimate the digital data-storage performance that would be realizable if it were possible to optimize the experimental arrangement to be more similar to a DFWM setup. The holographic contrast  $\Delta n$  by use of a data mask might be  $10^{-3}/2.5$ , accounting for the reduced fringe visibility.  $t_{\text{exp}}$  can be 200 ms with this material, and  $\tau_d$  can be 130 ms. A diffraction efficiency of 0.08 should be observed, and  $M\#$  therefore would be approximately 0.18, allowing 20 holograms to be stored. If all the best performance parameters achieved in the literature could be realized in the same device,  $M\#$  becomes approximately 0.6 when we use the same argument, enabling 67 stored holograms. Storage of  $1024 \times 1024$  pixel holograms would require a considerable increase in optical quality.

### 6. Assessment of Organic Photorefractives as Digital Storage Media and Future Research Required

The optical quality of this photorefractive polymer is good for 64-kbit hologram storage with a raw bit error rate of  $3.2 \times 10^{-4}$  and a scattered-light noise floor (the apparent diffraction efficiency that is due to scatter) of  $1.5 \times 10^{-5}$ . A previous study that used a photorefractive organic glass reported a raw bit error rate of  $<1.5 \times 10^{-5}$  from a material with a recording time of 500 s. The good optical quality, dynamic range, and the fast 2-s response speed demonstrated here for digital storage in our organic photorefractive represent a good overall performance for this polymer. For comparison, a typical photorefractive crystal, Fe-doped lithium niobate, has shown a raw bit error rate and scattered-light noise floor of  $3 \times 10^{-6}$  and  $4 \times 10^{-8}$ , respectively, at  $1064 \times 1064$  pixels with use of the same test equipment. PVK may have some partial crystallinity itself, and the exact nature of the aliphatic end group and sample prepa-

ration procedures affect the optical quality. Further detailed study of the material's optical quality properties and preparation procedures are necessary to provide avenues for optical quality improvement.

The maximum refractive-index modulation achieved in digital data storage was  $2.4 \times 10^{-5}$ , whereas  $10^{-3}$  can be achieved in a DFWM arrangement. To our knowledge, no digital data storage in organic photorefractives that have shown refractive-index modulations much higher than this in a DFWM arrangement has yet been demonstrated. The refractive-index modulation in lithium niobate is typically an order of magnitude lower, but in a much thicker device. The product of the refractive-index modulation and the sample thickness ultimately limits the number of stored holograms. The refractive-index modulation is limited by the nonlinear response of the material, the experimental arrangement, and possibly the photorefractive trap density that may limit the spatial-frequency response. The nature of the chromophore ultimately controls the birefringence and the nonlinear response of the material,<sup>27</sup> so chromophores with increased birefringence are needed that are also crystallization resistant.

The photorefractive trap density may ultimately limit the spatial-frequency response and therefore the refractive-index modulation in a digital storage arrangement. Photorefractive traps in this material are TNF anions,<sup>16</sup> and the corresponding positive charge resides on compensator sites. It is important therefore to study the nature of compensator sites.

The speed of response is controlled by several material and experimental parameters. Up to three material parameters are generally considered important: the optical sensitivity, the hole mobility, and the rotational diffusion rate of the chromophores. Digital data storage uses a lower intensity contrast during hologram recording than DFWM. Therefore, for digital data storage, the sensitivity is the important material property governing the response speed. In most fast organic photorefractive materials, the sensitivity limits the speed even in a DFWM arrangement.<sup>28</sup> According to Onsager's theory, the sensitivity is strongly electric field dependent in molecular systems, so the application of an electric field is an unavoidable prerequisite. Higher applied fields will yield faster response. Under fields of around  $50 \text{ V } \mu\text{m}^{-1}$ , the quantum efficiency of mobile hole generation is typically between 1% and 5% or lower. If this is improved, it will provide the most important method for speed enhancement. To date, the fastest organic photorefractives, reported to exhibit response times of approximately 1 ms in DFWM, have not been tested for digital data storage presumably because of limited optical quality in these materials. These materials will also inevitably have reduced speed in a digital storage arrangement because of less favorable experimental conditions.

The erasure characteristics of a stored hologram can be fitted to a biexponential decay in the DFWM arrangement. From an observed correlation in the

grating growth and erasure dynamics in these materials,<sup>16</sup> we can estimate the biexponential decay parameters for the case of the digital data-storage arrangement. The fast and slow decay time constants for grating erasure are estimated to be 1 and 12 s, with the relative amplitudes of the fast and slow components given by 0.7 and 0.3, respectively. Hence, in the case of the digital data-storage arrangement used here, these numbers can be used to estimate the time that would be required to erase a hologram to less than 2% of the initial refractive-index modulation; this value is 30 s. The dark lifetime of a hologram, which we define as the time required for its contrast to fall to 37% of its original value with all recording, reading, and erasure beams turned off in a DFWM arrangement, was 20 min.

## 7. Conclusions

In conclusion, digital holographic data storage was assessed in a photorefractive polymer composite showing high refractive-index modulation, fast speed, and good optical quality. Although the properties are not individually excellent, taken together they represent a high performance for an organic photorefractive and therefore are a good benchmark for digital data-storage performance in this class of materials. For the material studied, a raw bit error rate of  $3.2 \times 10^{-4}$  was observed along with a refractive-index modulation of  $2.5 \times 10^{-5}$  and a recording time of 2 s. The raw bit error rate and refractive-index modulation are comparable with previous reports of digital data storage in an organic photorefractive, and the speed is faster. This material is unsuitable for commercial digital data storage at this time, but future research into combining higher refractive-index modulation and speed with good optical quality, a larger useful aperture, and nondestructive readout, all in the same material, could result in useful performance levels.

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# ORGANIC STORAGE MEDIA FOR HOLOGRAPHIC OPTICAL MEMORY: STATE-OF-THE-ART AND FUTURE

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## ABSTRACTS

At present the main application of holography is the development of holographic optical memory with the super high information capacity. Recent advantages in decision of a number of technical problems associated with making holographic optical devices brought to the fore the question of the development of light-sensitive media for recording deep holograms. This paper presents the comparative analysis of the results concerning organic light-sensitive media of different types (photopolymerizable compositions, dichromated gelatin layers, photorefractive and photoanisotropic materials, etc.). It was shown that there are perspectives of the development of polymerizable materials based on photobleaching photochromogenic and photochromic photoinitiators for archive optical memory with high information capacity. The possibility of the development of working optical memory with the same information capacity is associated with expected advances in making photoanisotropic polymers containing photochromic fragments.

**Keywords:** holography, 3D optical memory, storage media, photochromism, photopolymer, gelatin

## 1. INTRODUCTION

Despite obvious progress in magnetic memory, interest in optical memory has quickened in the past years <sup>1</sup>. As a consequence of a wide practical implementation of optical disks, the development of volume (3D) optical memory to be used both in archive and working storage devices of ultrahigh capacity becomes a major problem. The 3D archive optical memory is now of greatest practical interest owing to the development of ultrahigh-capacity databases for telecommunications systems and space-system engineering.

The 3D optical memory is being developed in the following main directions <sup>2</sup>:

- (i) bitwise optical memory based on two-photon recording media <sup>3</sup> providing optical recording at any region of a bulk recording medium with focused laser radiation;
- (ii) bitwise optical memory based on frequency-selective recording media <sup>4</sup>;
- (iii) holographic optical memory <sup>5-9</sup>.

Holographic optical memory is unrivaled only in the realm of high-speed large-capacity parallel data processing systems <sup>8</sup>. Due to interference noise the storage density of a 3D multilayer holographic media can hardly be higher than  $10^{10}$  bit/cm<sup>3</sup>. An holographic storage system that combines both the spatial multiplexing of multilayer storage and wavelength multiplexing afforded by using volume holograms in order to produce significantly higher optical data capacity <sup>9</sup>. Research in these fields are being continued in competition with each other. Owing to the development of liquid-crystal spatial light modulators and arrays of radiation detectors, holographic optical memory devices seems to be now the most promising for practical applications. Bitwise 3D optical memory based on two-photon or frequency-selective recording media need a further development of laser technique including engineering parameters of femtosecond lasers and wavelength extension of acting laser radiation, respectively. The absence of light-sensitive recording media satisfying the current demand for 3D optical memory is a general problem of the above systems.

In this review, the results of development of organic recording media for holographic 3D memory are analyzed. Trends in the development of thick-layer self-developing media with a high angular selectivity of hologram recording received primary attention.

## 2. MEDIA FOR IRREVERSIBLE HOLOGRAM RECORDING

At the present time, archive optical memory of ultrahigh information capacity is of most practical importance. In this case, very high photographic speed is not a major requirement. A high resolving power of an organic photosensitive medium is of greater importance because it allows recording holograms on the areas of a minimal size (determined only by the wavelength of the recording radiation). The number of holograms recorded at the same spatial location is determined by the thickness-dependent angular selectivity of the recording and reconstruction as well as by diffraction efficiency (DE) of holograms. Note that high DE values are needed because DE determines the quality of holograms recorded at different angles of beams relative to normal. Based on these requirements, let us consider the properties of some irreversible recording media.

### 2.1 Layers with self-developing dichromated gelatin

In the past years, there is a great progress in improvement of the dichromated gelatin layers<sup>10</sup>. The development of thick self-developing layers containing glycerin as an additional component and capable of recording the real-time deep holograms without any processing<sup>11-21</sup> is of primary interest. DE of holograms recorded with He-Cd laser radiation ( $\lambda = 441.8$  nm) in a 0.5-mm thick layer containing 96 % glycerin exceeds 30 % and a photoinduced change in the refractive index is  $\Delta n = 2.5 \cdot 10^{-4}$  at exposures of  $\sim 10$  J/cm<sup>2</sup><sup>20</sup>. DE value increases on going to He-Ne laser ( $\lambda = 632.8$  nm) and on increasing concentration of ammonium dichromate. The light-sensitivity of such media to laser radiation of  $\lambda = 632.8$  nm can be increased up to 0.1 J/cm<sup>2</sup> by using Methylene blue as a sensitizer<sup>19</sup>. The angular selectivity for 2-mm thick layers is  $\sim 10'$ <sup>14</sup>. The storage time of recorded holograms is long but it still remains shorter than that required for archive optical memory.

### 2.2 Photopolymerizable systems

Photopolymerizable media include polymer layers containing photopolymerizable components or photocrosslinking groups<sup>10</sup>. The media of the latter type are systems based on poly(vinyl alcohol) or polyacryl acid sensitized with ammonium dichromate or dyes<sup>22</sup>. Introduction in dichromated polyacryl acid layers of electron-donating compounds such as dimethylformamide improves the sensitivity and DE of recorded holograms<sup>23</sup>. Holograms with DE = 85 % were recorded at exposures  $\sim 250$  mJ/cm<sup>2</sup> with Ar-laser radiation ( $\lambda = 488$  nm). In order to exclude the effect of reading radiation on holograms, the radiation of a Kr-laser ( $\lambda = 641$  nm) was used for readout. 20 holograms with an acceptable DE value were recorded at the same.

Of photopolymerizable systems, dry film recording media based on the radical polymerization of light-sensitive monomer-oligomer compositions have received much attention<sup>22</sup>. Analysis shows that they provide recording of phase holograms with DE = 100% at exposures 3–100 mJ/cm<sup>2</sup> by light in the range 440–680 nm in layers with a thickness of  $\sim 100$   $\mu$ m. As a rule, such systems require an additional dry post-exposure light or thermal processing. Unfortunately, studies on the possibility of using these systems for development of 3D holographic memory on optical disks<sup>24-27</sup> show that their information capacity must be improved. At date, it is shown experimentally that the surface density of information recording achieves 10 bits/ $\mu$ m<sup>2</sup> in a 100- $\mu$ m photopolymerizable layer<sup>24</sup>. Recently holograms of pages with capability about 480 Kbit were recorded in photopolymerizable layers with thickness of 250–500  $\mu$ m<sup>27</sup>. Despite the fact that such systems are promising for development of thick-film media, studies in this field are practically not being continued.

The study of photopolymerizable compositions based on acrylic monomers and a neutral component with low molecular weight is continued<sup>28-30</sup>. It was found the effect of polymer heterogeneity on holographic noise characteristics and resolution<sup>28</sup>. Changing the photopolymerization rate by either changing the initiator concentration or intensity of recording light beams allows to control the parameters of holographic media<sup>28</sup>. Light-sensitivity of the polymerizable compositions depends on interactions between polymer and the neutral component<sup>29</sup>. DE increases with a decrease of thermodynamic affinity of the polymer and the neutral component due to their high segregation and a consequent increase of the difference between refractive indexes of the produced phases<sup>30</sup>.

To increase the light sensitivity and storage time of recorded holograms and decrease the layer shrinkage in the course of photopolymerization, photopolymerizable compositions based on acrylamides and poly(vinyl alcohol) with special additives were suggested<sup>31</sup>. At the expense of optimization of the recording process, layer thickness and the content of acrylamide compositions holograms with DE = 80 % were recorded at exposition about  $E = 40$  mJ/cm<sup>2</sup><sup>32</sup>.

A low shrinkage is characteristic of the media based on siloxane monomers undergoing cationic photopolymerization<sup>33</sup>. For layers with  $d = 250 \text{ }\mu\text{m}$ , the photoinduced modulation of the refractive index exceeds  $\Delta n = 7 \cdot 10^{-3}$  at exposures of  $\sim 15 \text{ mJ/cm}^2$ . The absence of post-exposure processing, and sensitivity to oxygen as well as corresponding stability of recording characteristics are advantages of these systems as compared to media undergoing radical photopolymerization.

To extend the spectral sensitivity region to radiation of semiconductor lasers, media based on two-quantum photoinduced photopolymerization may be used<sup>34,35</sup>.

Using photobleaching dyes as photosensitizers, it is possible to record deep holograms in photopolymerizable media<sup>36</sup>. However, such media require an additional post-exposure treatment for obtaining the phase holograms. From this standpoint, media with a photochromic sensitizer are of the utmost interest<sup>37-41</sup>. In principle, two-quantum polymerization occurs in such media because for polymerization under the action of He-Ne laser ( $\lambda = 632.8 \text{ nm}$ ) to occur, the simultaneous illumination with noncoherent UV light is required. The UV light convert the initial colorless spiran form into the colored merocyanine one which in turn is the sensitizer of polymerization. The layers based on derivatives of triacrylate and iodine-substituted indoline spiropyranes exhibit the highest light-sensitivity in the presence of electron-donating organic compounds (triethylamine, triethanolamine, ammonium alkyltriphenylborates (co-initiators of polymerization)<sup>40, 41</sup>. Photopolymerization of acrylamide compositions proceeds effectively in the presence of a photochromic benzophenone-derivative of indoline spiropyran and triethanolamine<sup>38</sup>. Layers  $100\text{-}\mu\text{m}$  thick provide recording of holograms with  $\text{DE} = 80\%$  ( $\Delta n = 1.10^{-2}$ ) on spatial frequency  $\nu = 3000 \text{ mm}^{-1}$  at exposures  $100 \text{ mJ/cm}^2$ . The high DE values and nondestructive reconstruction of holograms are achieved by not only photopolymerization of monomer-oligomer compositions but also conversion of colored merocyanine form into the initial colorless form. The latter process occurs either spontaneously or under the action of visible light absorbed by the merocyanine dye. The possibility of recording deep holograms on these media is caused by photobleaching of the merocyanine form in the course of recording by laser radiation in the visible region.

Photopolymerizable compositions may be used for recording volume polarization holograms<sup>42</sup>

### 2. 3 Light-sensitive polymer media

In addition to the above-mentioned irreversible light-sensitive media based on photocrosslinking of molecular fragments and photopolymerization of monomer-oligomer systems, there is a number of materials whose sensitivity is determined by other chemical reactions.

Reoxan. Among other thick-film photosensitive polymer recording media, the so-called 'reoxan' is of the utmost interest. It is based on the photoinduced reaction of sensitized oxidation of anthracene molecules in a poly(methylmethacrylate) layer (with a thickness of up to several mm)<sup>43</sup>. The high DE values (up to 100%) at exposures  $\sim 1 \text{ J/cm}^2$ , considerable photoinduced change in the refractive index ( $\Delta n = 2 \cdot 10^{-2}$ ) over a wide (visible and IR) spectral region, spectral sensitivity region from UV to 900 nm are the advantages of this media. However, the dependence of holographic characteristics on the oxygen concentration and related pre- and post-exposure processing of layers make difficult practical applications of these recording media for holographic memory.

Media with photoinduced diffusion of components. A somewhat unexpected result of development of the reoxan-type media was the appearance of polymer systems whose parameters are determined by diffusion of a light-sensitive phenanthrenequinone, whereas distribution of its photoproduct, which is crosslinked to a polymer chain, is unchanged<sup>44-46</sup>. These results in an additional contribution into the modulation amplitude of medium refractive index that increases the DE values of recorded holograms. As a result of diffusion of the phenanthrenequinone molecules, a dark amplification of the refractive index and DE value of recorded holograms are observed<sup>44</sup>.

In order to diminish the duration of diffusion processes, this technique of the DE amplification was improved by using photochemically neutral molecules of a smaller size. The latter diffuse more easily in poly(methylmethacrylate) layers and react specifically with products of photochemical reaction<sup>47, 48</sup>. The molecules of a substituted anthracene (10 wt %) dimerizing under the action of light were used as a light-sensitive component, whereas chloroform was utilized as an inert component. As a result of interaction between the chloroform molecules and formed anthracene dimers, inversion of the phase contrast and a DE increase take place. The duration of the amplification process and the DE values of holograms were found to be temperature-dependent<sup>48</sup>.

These materials may have a thickness up to 5 mm. The optical disks base on these layers of the 1-5 mm thickness and a diameter from 2,5 to 10 cm were prepared. The hologram writing was produced by Ar-laser (488 nm). Laser radiation with  $\lambda=514$  or 532 nm may be used also but it requires more exposition<sup>49</sup>. Decreasing a diffusion time for components is achieved by post-exposition thermal processing at 55 °C. Holograms with DE=80 % were recorded in the layers of the 3 mm thickness<sup>50</sup>. At the same area of the medium were recorded up to 120 holograms binary pages.

### 3. REVERSIBLE RECORDING MEDIA

Replacement of high-cost electro-optical crystals (used for experimental proof of the possibility of development of holographic operative memory<sup>5,6</sup> by organic reversible recording media is a central practical problem in this field. Since the light sensitivity of the electro-optical crystals (as well as other self-developing recording media) is low, a search for thick-film organic light-sensitive materials with an acceptable DE, a long storage time of recorded holograms, high recyclability, and a short time for hologram recording and erasing is a main goal.

#### 3.1. Photochromic Materials

Being the most easy in fabrication and including compounds of different types, photochromic materials were considered for years as typical reversible holographic media<sup>51,52</sup>. Photochromic layers based on spiropyrans allow for hologram recording with DE > 10% at exposures of  $E = 60 \text{ mJ/cm}^2$  and  $E = 1 \text{ J/cm}^2$  by He-Cd ( $\lambda = 337.1 \text{ nm}$ ) and He-Ne ( $\lambda = 632.8 \text{ nm}$ ) lasers, respectively. As is known<sup>51</sup>, the recording of amplitude-phase holograms in amplitude photochromic materials is based on photoinduced modulation in the refractive index<sup>52</sup>. Unfortunately, a low recyclability of photochromic conversions and a limited storage time for recorded holograms typical for spiropyran-containing media prevents them from being used in operative optical memory. In this respect the layers based on derivatives of phenoxynaphthacenequinone, fulgides, diarylethylenes and thioindigo dyes seem to be more promising. However, they receive yet no wide recognition. The reason appears to be relatively low values for the obtained DE<sup>52</sup>.

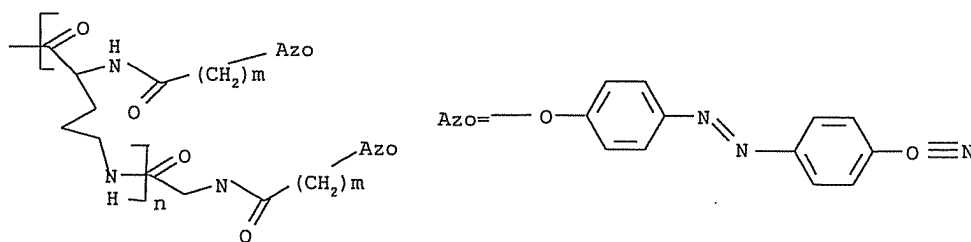
More recent studies on photochromic compounds<sup>31,53-55</sup> have confirmed in general the earlier conclusions. In addition, the sensitivity of layers based on spiroxazines and poly(*N*-vinyl carbazole) to radiation of He-Ne laser ( $\lambda = 632.8 \text{ nm}$ ) was increased up to  $300 \text{ mJ/cm}^2$ <sup>53</sup>. It was shown that the sensitivity of spiroxazine-based materials (with a recyclability higher by more than two orders of magnitude than that for spiropyran-based materials) depends on the methods of their photoactivation and hologram recording<sup>56</sup>. Photochromic materials based on azo dyes are of great interest<sup>57</sup>. They exhibit a unique recyclability owing to the fact that their photochromic conversion includes *cis-trans* photoisomerization. In addition, holograms in such systems can be intensified by illumination with a noncoherent light<sup>58,59</sup>. The theoretical analysis and experimental results show that a weak nonresonant preexcited light can be used for realize dynamic holographic storage<sup>60</sup>. As a result the wavelength range of optical storage is extended and the intensity of the writing beams is reduced.

The above-mentioned results are typical of films with a thickness of less than 100  $\mu\text{m}$ . However, it is possible to increase the information capacity by increasing the film thickness<sup>61</sup>. The change in the thickness from 16  $\mu\text{m}$  to 1 mm results in a significant increase of angular selectivity of recording (at the same value of photoinduced optical density)<sup>61</sup>. Theoretically, it is possible to record about 100 holograms at the same location of the photochromic film. Experimentally, 48 holograms with DE = 0.1% of binary transparencies with a capacity of  $10^4$  bits were recorded on the area  $1 \text{ mm}^2$  (mean spatial frequency of recording  $\nu = 2000 \text{ cm}^{-1}$ )

#### 3.2 Photoanisotropic recording media

The phenomenon of photoinduced anisotropy (birefringence) in polymer photosensitive layers<sup>62,63</sup> opens up possibilities for development of photoanisotropic organic recording media which are of specific interest for polarization holography<sup>64</sup>.

In principle, the use of photoanisotropic media (in particular, films based on poly(vinyl alcohol) and photochromic azo dyes<sup>65</sup> allows one to double (as compared to other materials) the number of holograms recorded at the same location of a photosensitive layer with the same spatial frequency by varying the polarization of recording light. The use of only one laser radiation with mutually perpendicular polarization for recording and readout of holograms as well as nondestructive readout beyond the absorption band is the advantages of these materials. For polarization holograms recorded in layers based on poly(methylmethacrylate) and an azo dye, the DE value attains 35%<sup>66</sup>.



To increase the value of photoinduced birefringence and DE of recorded holograms, azo dyes may be introduced as the side flexible fragments of polymer chains of mesomorphic polyesters<sup>67-74</sup> or oligopeptides<sup>75, 76</sup> (see the scheme). This results in increasing DE as the oligomer size ( $n$ ) increases and in decreasing DE as the number of methylene groups ( $m$ ) increases. The storage time increases (up to 1 year) owing to aggregation of photoinduced forms<sup>75</sup>, whereas the high recyclability (more than  $10^4$ ) is retained. In the case of photochromic oligopeptides, holograms with DE = 76% were recorded with a linearly polarized radiation of an Ar laser ( $\lambda = 488$  nm,  $I = 2$  W/cm<sup>2</sup>) and readout with circular-polarized radiation of a He-Ne laser ( $\lambda = 632.8$  nm,  $I = 4.2$  mW). Erasure of holograms may be performed either by heating or by illumination with a UV laser ( $\lambda = 351$  nm). Recorded holograms may be also erased with a circular-polarized laser radiation. Increasing the rigidity of peptides backbone is crucial in the design of effective azobenzene peptides for optical recording<sup>76</sup>.

### 3. 3 Photorefractive polymer layers

As a consequence of development of holographic memory based on electro-optical crystals [8], search for photorefractive polymers, in which holograms may be recorded on inserting in an external electric field, is being continued<sup>77-82</sup>. The following two effects are used: (i) photoassisted poling of molecules in an external electric field and (ii) photoinduced redistribution of the electron density (as in electro-optical crystals). The media of the first type have attracted the most notice. Recording media of this type based on poly(*N*-vinyl carbazole) with trinitrotoluene and an azo dye provide recording with DE = 100% at an external field strength of 90 V/ $\mu$ m owing to photoinduced refractive index modulation as large as  $\Delta n = 7 \cdot 10^{-3}$  under the action of laser radiation with an intensity of 1 W/cm<sup>2</sup><sup>77</sup>.

The dark decay of holograms depends on the dark conductivity<sup>83</sup>. Incorporating sensitizers or more charge transport segments leads to more dark decay because of increasing dark conductivity. The dark hologram decay at elevated temperatures can also be increased by the thermal stimulated discharge current spectroscopy technique.

In photorefractive media based on poly(methylmethacrylate), nitrobenzimidazoline and fullerene<sup>84</sup>, holograms with a capacity of 64 Kbit, DE = 7% and reading error of  $1.5 \cdot 10^{-5}$  were recorded<sup>85</sup>. These holograms may be stored for more than 300 h without any changes<sup>84, 86</sup>. The recording time (usually about 0.5 s<sup>79</sup>) may be reduced by optimization of the external electric field strength and intensity of recording laser beam<sup>87</sup>.

Most of the holographic parameters of the photorefractive polymer layers exceed those typical of known electro-optical crystals. The developed polymers can be used in holographic memory devices in conjunction with semiconductor lasers having lower powers than lasers used for recording in the electro-optical crystals. Unfortunately, the thickness of photorefractive polymer layers is relatively small (usually < 100  $\mu$ m) that leads to a moderate angular selectivity (> 0.5°). At a maximal obtained angular selectivity (~1°), only 10 holograms may be recorded at a location<sup>85</sup>.

### 3. 4 Media with photochemical spectral hole burning

The fundamental possibility of development of ultrahigh-capacity holographic memory concerns the use of photoburning of spectral holes. Note that this phenomenon is observed only at very low temperatures<sup>88-90</sup>. Holograms recorded at 4.2 K in layers ( $d = 0.5$ – $0.9$  mm) based on derivatives of anthraquinone or porphyrine in different polymer binders exhibit DE  $\leq 0.2\%$  at exposures  $\geq 0.1$  J/cm<sup>2</sup><sup>88</sup>. While the predicted limit for the frequency-selective holograms recorded at the same location is of about 800, only about 100 images have been recorded in practice. Note that it is possible to record about 6000 holograms (limiting value is 12000)<sup>89</sup> in poly(vinylbutyral) layers containing chlorine (C<sub>20</sub>H<sub>16</sub>N<sub>4</sub>)<sup>90</sup>.

## 4. CONCLUSIONS

The table lists the ultimate characteristics of the above-mentioned holographic light-sensitive recording media.

Table . Limiting measured parameters of organic recording media for holographic memory

Recording medium	$\Delta\lambda$ , nm	$S$ , mJ/cm <sup>2</sup>	DE, %	$t_{\text{storage}}$	$\Delta\Theta$	$d$ , mm	$N$ , cycles	Additional processing
Irreversible recording media								
Dichromated gelatin	400-680	0.1	100	3 months	min	3.0	-	No
Photopolymerizable media	400-680	3.0	100	Unlimited	grad	0.5	-	Yes
Reoxan	400-900	500.0	100	Unlimited	min	5.0	-	Yes
Media with photoinduced diffusion	400-680	100.0	80	Unlimited	min	5.0	-	No
Reversible recording media								
Photochromic material	300-650	50.0	<	Unlimited	min	10.0	Unlimited	No
Photoanisotropic media	350-650	100.0	15	Unlimited	min	1.0	Unlimited	No
Photorefractive polymer layers	400-650	100.0	100 100	?	grad	0.1	Unlimited	No

Remarks:  $\Delta\lambda$  is the region of spectral sensitivity;  $S$  is the holographic light-sensitivity;  $t_{\text{storage}}$  is the storage time of recorded holograms;  $\Delta\Theta$  is the angular selectivity of hologram recording;  $d$  is the thickness of a recording medium;  $N$  is the recyclability; 'additional processing' means that either preexposure or postexposure processing is needed.

To obtain a holographic memory with a high information capacity, organic recording media must exhibit not only an adequate sensitivity and high DE, but also the possibility of recording a great number of holograms at each spatial location. In principle, this can be achieved at a high angular or/and frequency selectivity of recording and readout processes. Analysis of the presented data shows that the desired information capacity of holographic memory can be achieved by means of frequency-selective recording in dye-containing organic polymer media that provide the photoburning of spectral holes. Unfortunately, such a memory can be realized only at very low temperatures.

Thick-layer recording media providing a high angular selectivity of hologram recording are more acceptable from the practical viewpoint. Among known irreversible media, photopolymerizable layers containing photobleaching dyes or photochromic sensitizers are most promising. Such media allow the recording of deep holograms without additional processing usually needed for obtaining holograms with a high DE. Polymer layers with photoinduced diffusion of neutral components, which react with photoproducts formed in a polymer matrix, seem to be also promising. Self-developing layers of dichromated gelatin may be used for developing archive holographic memory. However, a poor reproducibility of their properties and a relatively low storage time of recorded holograms can restrict wide application of these systems.

Of reversible recording media, photoanisotropic organic materials exhibit the most reasonable properties. They can provide the desired angular selectivity and high DE. However, in this case it is necessary to diminish the time of recording. In certain cases, when high DE is not needed, organic photochromic materials may be utilized. Photorefractive polymer layers appear to be very promising. However, they have relatively small thickness and therefore can provide hologram recording only with a low selectivity. At present, they cannot therefore compete with electro-optical crystals.

It should be noted that all the above-mentioned recording media are characterized by a relatively low sensitivity. This makes the development of holographic memory devices more complicated.

Undoubtedly, further advancement of organic recording media can be expected in the near future because development of ultrahigh-capacity holographic memory is one of the hottest areas in current research.

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# PHYSICAL REVIEW B

## CONDENSED MATTER AND MATERIALS PHYSICS

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### RAPID COMMUNICATIONS

*Rapid Communications are intended for the accelerated publication of important new results and are therefore given priority treatment both in the editorial office and in production. A Rapid Communication in Physical Review B may be no longer than four printed pages and must be accompanied by an abstract. Page proofs are sent to authors.*

#### Holographic storage in conjugated-polymer composites

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We report on holographic storage with relatively high diffraction efficiencies in films ( $2\text{ }\mu\text{m}$  to  $20\text{ }\mu\text{m}$  thick) of conjugated polymer/glass and conjugated polymer/polymer composites with emphasis on the former. An index of refraction change  $\Delta n$  as high as  $8.6 \times 10^{-3}$  was obtained. The grating formation was attributed primarily to the photochromic effect. However, the anomalous large two-beam coupling that was observed in these materials cannot be explained by a photochromic mechanism. This, together with the small nonlinear electro-optic coefficient  $r_{\text{eff}} = 0.42\text{ pm/V}$  may suggest that a weak photorefractive process also contributes to the hologram formation in these materials. Holograms written on these conjugated polymer composite films are stable in the dark for (at least) one year. [S0163-1829(98)50420-1]

Organic-based holographic storage has been a subject of considerable interest in the last few years. Both photorefractive<sup>1-3</sup> and photochromic<sup>4</sup> organic materials were considered for this application. The former class of materials has yielded mostly reversible holograms, but required poling under a high external electric field, whereas the latter yielded nonreversible holograms but did not require any inherent order. In both cases the high diffraction efficiency that was obtained was attributed to the large index change that was induced in the material. We report here on holographic storage in composites of conjugated polymers, namely, functionalized poly(*p*-phenylene vinylene), PPhydroxyV, in zirconia glass (polymer/glass) or in nonconjugated polymer polyvinyl alcohol (polymer/polymer) with emphasis on the former. Both classes of materials show a relatively high index of refraction change, and an unusual high two-beam coupling phenomena, both without the need of external electric field.

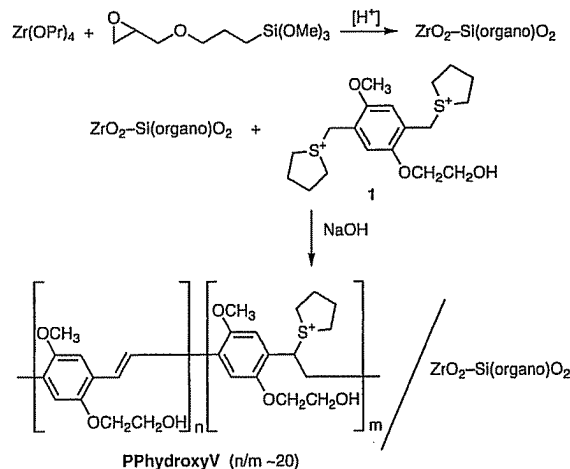


FIG. 1. The preparation of polymer/glass composites.

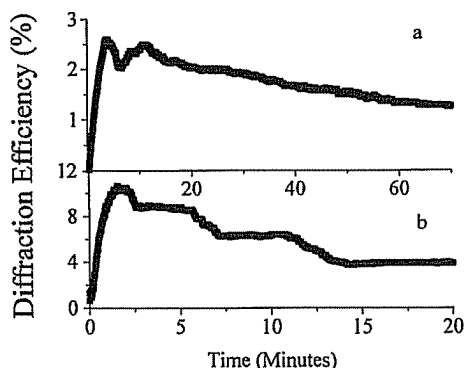


FIG. 2. Diffraction efficiencies vs time for a 2.5- $\mu\text{m}$ -thick polymer/glass film (a), and for a 20- $\mu\text{m}$ -thick polymer/polymer film (b).

Previous reports of holographic storage in composites of  $\text{PPVN}_2\text{O}_5$  thin sol-gel films were written by strong laser pulses, and were attributed to surface relief.<sup>5</sup> Another study reports on photorefractive effects in a conjugated polymeric mixture.<sup>6</sup> In this paper we show that conjugated polymer can be used for grating writing and the formation of phase holograms with relatively high efficiencies and long-term stability.

The polymer/glass composites were prepared by polymerizing a functionalized bis-sulfonium salt, **1**, with an aqueous base within a mixed gel of zirconia and 3-glycidoxypolypropylsilica to produce upon drying at room temperature a  $\sim 21$  wt % functionalized poly(*p*-phenylene vinylene) polymer, PPhydroxyV, in the zirconia-organosilica glass (Fig. 1). The described combination of zirconia and 3-glycidoxypolypropylsilica was used for its superior crack resistance to aqueous base in the polymerization process.<sup>7</sup> Similar base polymerization was used also to prepare the composites of polyvinyl alcohol (PVA) and PPhydroxyV. The thickness of the polymer/glass films ranged between 1 and 4  $\mu\text{m}$  and that of the polymer/polymer films ranged between 5 and 20  $\mu\text{m}$ . A grating with a spacing of 1.65  $\mu\text{m}$  was written using two beams with incident intensity of 0.8  $\text{W}/\text{cm}^2$  at 514 nm. Diffraction efficiencies were monitored in parallel to the grating formation using a probe read beam at 532 nm and are shown in Fig. 2. Maximum diffraction efficiencies of 2.5% for the 2.5- $\mu\text{m}$ -thick polymer/glass film [shown in Fig. 2(a)] and 10% for the 20- $\mu\text{m}$ -thick polymer/polymer film [shown in Fig. 2(b)] were obtained. The diffraction efficiencies are a

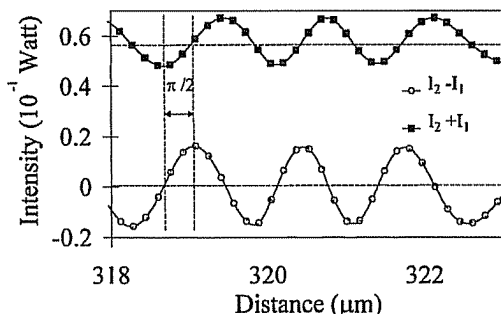


FIG. 3. The sum and difference of the outcoming writing beams  $I_1$  and  $I_2$  as a function of the grating displacement for a 2.5- $\mu\text{m}$ -thick polymer/glass film.

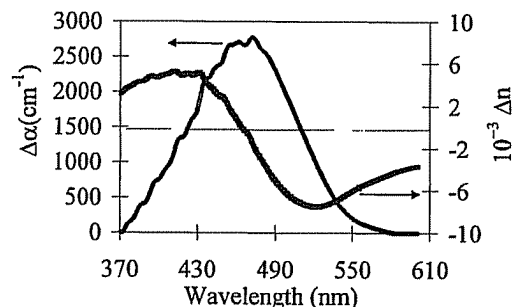


FIG. 4. The measured value of  $\Delta\alpha(\lambda)$  for a polymer/glass film as well as  $\Delta n(\lambda)$  derived from  $\Delta\alpha(\lambda)$  via the Kramers-Kronig relations.

*priori* attributed to the formation of both phase grating and an absorption grating. Holograms written on these conjugated polymer/glass and conjugated polymer/polymer composite films are stable in the dark for (at least) one year.

A quantitative assessment of the respective contribution to the diffraction from the refractive index (phase) grating, and the absorption grating was obtained by applying the displaced grating method.<sup>8</sup> Consider  $I_+$  and  $I_-$ , which are the sum and difference of the outcoming light beams, respectively. It was shown that a translation of the grating orthogonal to the beams bisector introduces a phase shift in proportion to the grating displacement  $\zeta$ . In terms of the amplitudes  $A$  and  $P$ , and the phase shifts  $\phi_P$  and  $\phi_A$  of the refractive index and the absorption gratings, respectively,  $I_+$  and  $I_-$  are given by

$$I_+ = I_1 + I_2 = I_0 \exp(-\alpha_0 d / \cos \theta) [2 - 4A \cos(\phi_A + 2\pi\zeta/\Lambda)],$$

$$I_- = I_1 - I_2 = I_0 \exp(-\alpha_0 d / \cos \theta) [0 - 4P \sin(\phi_P + 2\pi\zeta/\Lambda)], \quad (1)$$

where  $2\theta$  is the angle between the writing beams, and  $d$  is the sample thickness. A typical measurement of  $I_+$  and  $I_-$  of the two outcoming writing beams vs the grating displacement  $\zeta$ , is presented in Fig. 3. The measurement was done after 5 min of writing on a 2.5- $\mu\text{m}$ -thick polymer/glass composite film at the conditions described above. The amplitudes of the index grating and absorption grating as derived from these measurements were  $\Delta n = 8.6 \times 10^{-3}$  and  $\Delta\alpha = 1290 \text{ cm}^{-1}$ , respectively. Note that the results indicate clearly that the phase (refractive index) grating is in phase with the absorption grating.

Kramers-Kronig relations<sup>9</sup> were used to calculate the index of refraction change due to the absorption change of the polymer/glass composite films (Fig. 4). The wavelength response of the absorption spectra  $\Delta\alpha(\lambda)$  was measured separately and was used for the calculation of the index of refraction change  $\Delta n(\lambda)$ . It was found that the maximum index of refraction change occurs at 525 nm, and  $\Delta n$  as high as  $7.4 \times 10^{-3}$  and  $7.2 \times 10^{-3}$  were obtained for the writing (514 nm) and the reading (532 nm) wavelengths, respectively. It can be concluded that the main contribution to the large index of refraction change is due to a photochromic process that induces a large index modulation through the Kramers-Kronig relations. The slow formation of the grating as well

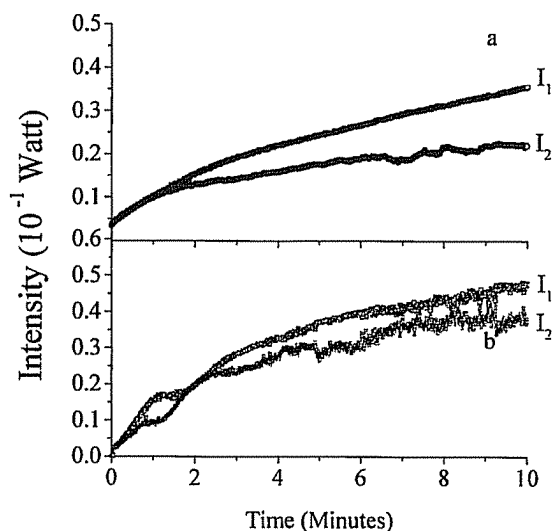


FIG. 5. The time evolution of the outgoing writing beam intensities  $I_1$  and  $I_2$  during the grating formation for a 2.5- $\mu\text{m}$ -thin polymer/glass film (a), and for a 14- $\mu\text{m}$ -thick polymer/polymer film (b).

as the zero phase shift between the absorption and index gratings, also support a photochromic mechanism for the grating formation. Calculating<sup>10</sup> the relative contribution of the index of refraction and absorption gratings to the diffraction efficiency based on the measured  $\Delta n$ ,  $\Delta\alpha$  for the polymer/glass composite films gives  $\eta(\Delta n)=1.71\%$  and  $\eta(\Delta\alpha)=0.67\%$ . This result is in good agreement with the measured diffraction efficiency shown in Fig. 2(a).

Unique to this type of materials is the observation of two-beam coupling phenomena during the holograms' formation process. Consider Figs. 5(a) and 5(b), in which the time evolution of the beam intensities  $I_1$  and  $I_2$  during the grating formation is shown for a 2.5  $\mu\text{m}$ -thin polymer/glass film and for a 14- $\mu\text{m}$ -thick polymer/polymer film, respectively. A strong energy transfer between  $I_1$  and  $I_2$  is clearly observed. In the 2.5- $\mu\text{m}$  polymer/glass film, after approximately 2.5 min of writing the beam intensities, which were initially equal, change and  $I_1$  become more powerful. (Recall that the grating formation is accompanied by a uniform bleaching that causes a monotonic uniform increase of the transmission.) In the 14- $\mu\text{m}$ -thick polymer/polymer film several consecutive cycles of the energy exchange were observed, in addition to oscillations of the intensity between the two beams with period of a few seconds. By applying the displaced grating method several times during the hologram formation it was observed that the direction of the energy transfer was correlated with the sign of  $I_-$ . This behavior is not typical of conventional photochromic holographic storage media. Therefore, special care was given to verify that these phenomena were not artifacts due to experimental error such as instability of the setup, and were completely reproducible.

Following Ref. 11, when the condition  $\lambda d/\Lambda^2 \gg 1/2\pi$  is met, the hologram is a thick hologram, where  $\lambda$  is the read wavelength, and  $\Lambda$  is the grating fringe spacing. Therefore, the 2.5- $\mu\text{m}$ -thin polymer/glass film should be regarded as a thin Raman Nath regime hologram, whereas the 14- $\mu\text{m}$ -thick polymer/polymer film should be regarded as a thick Bragg

regime hologram. Using standard formalism<sup>11</sup> developed originally for thick films, we have calculated a two-beam coupling gain coefficient  $\Gamma$  for the thin film in Fig. 5(a) to be  $1765\text{ cm}^{-1}$ . Other thin polymer/glass film values range between 900 and  $1400\text{ cm}^{-1}$ . These values in thin holograms do not imply that the intensity will be exponentially growing upon transmission via these holograms since this occurs in thick holograms with the incoming beam ratio  $\beta=I_1/I_2 \gg 1$ ,<sup>11</sup> but rather show that in a very thin grating a considerable amount of energy is transferred between the two incoming beams with equal intensity. However, in a thick polymer/polymer film the use of  $\Gamma$  is correct. The calculated gain coefficient  $\Gamma$  for the 14- $\mu\text{m}$ -thick polymer/polymer film shown in Fig. 5(b) yields  $315\text{ cm}^{-1}$ . Beam intensities after passing the film were measured for more than 5 h, and intensity exchange continued over the entire time measured for the 2.5- $\mu\text{m}$ -thin polymer/glass film, indicating that photo-degradation of the film does not play a major role in the coupling mechanism. We have observed beam coupling at the writing beam intensity ratio  $\beta=1$  for both thin and thick holograms. It occurred even when the diffraction efficiency was as low as 0.1% for thin films and as high as 10% for the thick polymer/polymer films. An interesting feature of these phenomena was that when the concentration of the conjugated polymer within the polymer/glass sol-gel composites was strongly increased, the diffraction efficiency was increased and the beam interaction and the energy exchange were inhibited.

As pointed out above, the beam coupling behavior observed by our group is not a typical behavior of a photochromic material. Beam coupling can occur only when there is a phase shift between the diffracting grating and the interference grating. In a normal photochromic material there is no phase shift between the interference grating and the absorption grating. A similar phenomenon was observed in a thermal grating formation by a  $\text{CO}_2$  laser in a liquid crystal layer.<sup>12,13</sup> In this case the grating is local in nature and has no phase shift between the intensity and the index of refraction gratings. The origin of the beam coupling is attributed to an interference of the newly produced diffraction orders with the original incoming beams producing a secondary grating. The beam exchange was for a large intensity ratio  $\beta$ . This mechanism can exist when a relatively large diffraction efficiency is produced by the grating and fails to explain our observation of beam exchange even in the case of very low diffraction efficiencies [Fig. 5(a)]. Moreover, it cannot explain the observation of the large two-beam coupling gain in the thick films with  $\beta=1$  where the Bragg condition is met and no higher order diffraction orders are observed. Other studies<sup>4</sup> obtained with a thick photochromic material showed that in the case of a large intensity ratio  $\beta$ , a phase shift between the intensity and the index of refraction gratings may occur due to self-diffraction of the incoming beam through the formed grating. This mechanism as well fails to explain how a beam exchange is observed in thin films of polymer/glass for  $\beta=1$ . Moreover, the phase shift should have been observed in the displaced grating experiment, where it was observed that there is no phase shift between the phase grating and the absorption grating.

Two-beam coupling is usually attributed to photorefractivity. Key components in any photorefractive material are photoconductivity and electro-optic effects. The electro-optic effect was measured by inserting a sample film between two perpendicular polarizers.<sup>11,14</sup> An ac voltage up to 400 V rms was applied to the sample while the intensity change was detected with a Si detector and a lock-in amplifier. An effective electro-optic coefficient  $r_{\text{eff}}$  of 0.42 pm/V was measured, somewhat small compared to previous studies of organic photorefractive materials. Moreover, using the displaced grating method we were not able to measure a 90° shifted component of the index of refraction grating

with respect to the intensity grating. Therefore the main contribution to the grating formation is not likely to be photorefractive.

In conclusion, we have shown an application for conjugated polymeric materials as the active component within holograms. The high index of refraction obtained in our studies is attributed mainly to a photochromic effect. The beam coupling and the energy exchange between the beams, which is not usually shown in photochromic materials, is not fully understood at present.

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